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Formulation and Performance Studies of Polymer Bonded Explosives (PBX) Containing Energetic Binder Systems. Part I

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ABSTRACT

In an effort to comply with Insensitive Munitions (IM) criteria together with the expectation of increasing the warhead performance against specified targets, two part energetic binder systems comprising an energetic polymer and plasticiser that offer promise for future use in PBX (polymer bonded explosive) fills in high performance, tactical missiles have been investigated. Warhead fills within modern missiles such as ASRAAM (Advanced Short Range Air-to-Air Missiles) typically contain cast-cured PBXs comprising high energetics loadings in an inert binder matrix. The use of the inert binder, which comprises around 20% of the final formulation, dilutes the final energy output of the PBX. To this end, several energetic binder formulations have been developed that may offer potential use in ASRAAM type missiles. By use of energetic binders systems comprising polyGLYN and K10 or GLYN oligomer plasticiser, increases in performance parameters were observed. This technical report details the formulation of several PBXs developed to maximise casting density and processibility for potential use in ASRAAM warheads that may offer improved IM properties.

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Executive Summary

In an effort to comply with Insensitive Munitions (IM) criteria, energetic binder systems comprising an energetic polymer and plasticiser, are being developed for future use in PBX (polymer bonded explosive) fills for high performance, tactical missiles. Modern warhead fills such as ASRAAM (Advanced Short Range Air-to-Air Missiles) typically contain cast-cured PBXs comprising a high energetics loading with inert binders. The use of the inert binder dilutes the final energy output of the PBX, however if energetic binders are used, the final energy output should be improved. Increased warhead performance will be observed as the extra energy arising from the energetic binder will increase fragmentation and enhance blast. Probability of kill is likely to be increased without compromising the IM properties required for munitions. To this end, several possible formulations have been developed that may offer potential use in ASRAAM warheads in the near future.

PBX formulations were developed to maximise explosive performance, and were evaluated by velocity of detonation and detonation pressure measurements. These tests demonstrate the ability of energetic binders to improve processing and performance over conventional inert PBXs. By the use of energetic binders, increases in performance were observed. Finally, this technical report details several recommendations for future work.

Authors

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Arthur Provatas graduated with a PhD (Chem. Tech.) from the University of South Australia in 1997 in polymer chemistry and commenced work for the Explosives Group, Weapons System Division of DSTO investigating energetic polymers as binders, polymer bonded explosives for military applications. Dr Provatas is the Chemical Safety Officer for WSD and the Focus Officer for environmental issues with TTCP (The Technical Cooperation Program, KTA 4-28). Dr Provatas' multidisciplinary research has led him to publish research in polymer science, inorganic chemistry, chemical engineering, surface chemistry and organic synthesis

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Abbreviations

ADF	Australian Defence Force
BDNPA/F	Bis-dinitropropylacetal/formal
DBTDL	Dibutyltin Dilaurate
DOS	Dioctyl Sebacate
DSC	Differential Scanning Calorimetry
F of I	Figure of Insensitiveness
GAP	Glycidyl Azide Polymer
GLYN	Glycidyl Nitrate or 2-nitratomethyloxirane
HTPB	Hydroxyl Terminated Polybutadiene
HMX	Cyclotetramethylenetetranitramine
IDP	Isodecyl Pelargonate
IM	Insensitive Munitions
IPDI	Isophorone Diisocyanate
K10	Dinitroethylbenzene and trinitroethylbenzene in a 65/35 ratio
NENA	Nitrato Ethyl Nitramine
NMMO	2-Nitratomethyl-3-methyloxetane
PBX	Polymer Bonded Explosives
P_{CJ}	Chapman-Jouguet (Detonation) Pressure
PolyGLYN	Polymer of 2-nitratomethyloxirane
PolyNIMMO	Polymer of 3-nitratomethyl-3-methyloxetane
RDX	Cyclotrimethylenetrinitramine
Tg	Glass Transition Temperature
Tm	Melting Temperature
T of I	Temperature of Ignition
VoD	Velocity of Detonation

1. Introduction

The need for Insensitive Munitions has arisen from a number of accidents involving ordnance use and storage. Some of these accidents have been catastrophic with great loss of life, operational effectiveness and severe damage to expensive and important platforms and equipment [1]. Insensitive Munitions (IM) are defined as "...those munitions which reliably fulfil their performance, readiness and operational requirements on demand, but in which the violence of the response to unplanned hazardous stimuli is restricted to an acceptable level determined by (specified) test and response criteria" [2]. The Australian policy additionally states "IM are to be introduced into service with the Australian Defence Organisation, where it is sensible, practicable and cost-effective to do so".

In support of this policy, DSTO has initiated research into low sensitivity, polymer bonded explosive (PBX) based ordnance, which contains energetic binders as a replacement for inert binder systems. Such PBX technology involves cast-cured isocyanate cross-linked systems, typically polyurethanes, that provide a means for reducing sensitivity to hazardous stimuli while maintaining or enhancing warhead performance. PBXs with an energetic binder system comprising a nitrato functional polyether, polyGLYN with an energetic oxidant have been investigated as these systems should offer both excellent IM properties and warhead performance.

The work described in this report covers the formulation of energetic binder systems with high loadings of RDX, the processing parameters, and performance assessment including velocity of detonation and detonation pressures. Compatibility tests and physico-chemical testing of the PBXs are also reported.

A common problem for cast-cured PBXs is exudation of small molecule plasticisers from the polymer matrix leading to sensitised zones in the PBX and potentially hazardous consequences. In this context, two plasticisers of differing nature were trialed in PBX formulations. The plasticisers, K10 and GLYN oligomer were both formulated in PBX with high loadings of RDX. The GLYN oligomer is hoped to offer slower migration through the PBX matrix because of its similar structure and affinity with the parent polymer - polyGLYN.

This report is the first publication arising from air force task AIR 01/069 'Advanced Explosives for Air-Launched Missile Warheads'. The task anticipates that in the near future, missiles such as ASRAAM (Advance Short Range Air-to-Air Missiles) may require improvements to better enable IM compliance and improve warhead performance (kill probability against designated targets). The use of energetic binders in PBX formulations may very well offer potential application as fills in the ASRAAM warhead in the future.

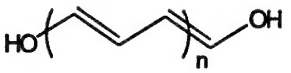
2. Background

Binders are polymeric compositions, which act to hold fuels and oxidisers within a desensitised matrix and confer IM properties.

Binder = polymer + plasticiser(s).

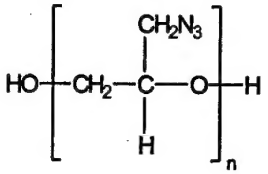
Binders impart to PBXs a lowering of vulnerability, contributing to the development of insensitive munitions, IM. Current PBXs contain binders that possess good dimensional stability and required energy absorbing properties, but are difficult to recover or recycle during manufacture or demilitarisation.Additionally, these binders are inert and offer no energy contribution to the final PBX formulation. Energetic binders are polymers which contain *explosophoric* chemical groups such as nitro (C-NO_2), nitramine (N-NO_2), difluoroamino (-NF_2), azido groups (N_3), and nitrate esters (-ONO_2). Incorporation of these binders in PBXs offers energy increases above those obtainable with inert binders like hydroxy-terminated polybutadiene (HTPB), without any concomitant loss in PBX mechanical properties.
Figure 1 highlights various energetic binders, including glycidyl azide polymer (GAP), the nitrato polyethers like poly(3-nitratomethyl-3-methyloxetane) (polyNIMMO), and poly(glycidyl nitrate) (polyGLYN). Other energetic binders include thermoplastic elastomers (TPE & ETPE), fluoropolymers, polyvinylnitrates, polynitroaromatics, *N,N*-bonded epoxy functional polymers, and nitrated polybutadienes like NHTPB.

Inert polymers

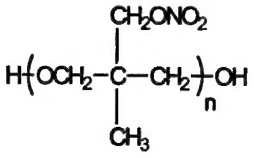


HTPB

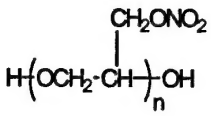
Energetic polymers



GAP



PolyNIMMO



PolyGLYN

Figure 1: Typical Inert and Energetic Binders

Energetic plasticisers include oligomers of the polymers mentioned above (short chain polymers having number average molecular weights ranging from 200 to 800), as well as a wide variety of nitrate esters, nitroaromatics and azido plasticisers. Plasticizers serve to enhance the stability and mechanical properties of PBXs, acting to (1) ease processing and lower viscosity, (2) modify mechanical properties (lower the glass transition temperature, T_g), (3) improve safety, and (4) provide energy or modify oxygen balance to a PBX.

3. Experimental

Current energetic binder materials are relatively expensive and thus better suited for fills in high cost, high performance weapon systems that have volume and number restrictions on the warhead. At WSD we have formulated several cast-cured PBXs that have potential as an IM fill for missile warheads. The formulations contain RDX as the oxidant fill with a bimodal RDX distribution of 60/40 Type A/E used to maximize casting density. All PBXs contained polyGLYN as the binder available for reaction with the isocyanate cross-linking agents, IPDI and Desmodur N100. The energetic plasticisers K10 and GLYN oligomer (at a polymer to plasticiser ratio of 50:50), were both trialed in PBX formulations to gauge plasticiser mobility. K10 is a mixture of dinitroethylbenzene and trinitroethylbenzene in a 65/35 ratio and is a flammable and toxic material (DG Class 6.1). The GLYN oligomer was provided under collaborative agreement with the UK, whereby the UK supplied DSTO with a research quantity of the new energetic plasticiser. The oligomeric version of the parent polymer, polyGLYN, should offer improved plasticisation properties, good energy output, good mechanical properties and low exudation or migration of plasticiser from the binder system. All PBX formulations have been designated using Australian PBX nomenclature (e.g. ARX-3005 M1, see Appendix A).

3.1 Binder Ingredients

PolyGLYN and GLYN oligomer were obtained from ICI Nobel Enterprises (Ardeer, Scotland) and degassed for 16 h prior to use. For polyGLYN, Batch 31 was used as received and had a hydroxyl value of 56.1 mg KOH/g. The GLYN oligomer was shipped as a 5% solution of plasticiser in dichloromethane and the solvent was removed under vacuum to leave a yellow fluid corresponding to the GLYN oligomer. Isocyanate curing agent isophorone diisocyanate (IPDI) was obtained from Bayer and distilled under reduced pressure to give a clear product. Desmodur N100, a polyfunctional isocyanate (functionality of 2.3), was also obtained from Bayer and used as received. Dibutyl tin dilaurate (DBDTL) is a cure-accelerating catalyst obtained from Aldrich and was used as received.

3.2 RDX

RDX Type 1 (Woolwich), Grades A and E [3] were received from ADI Ltd, Mulwala. RDX grades were received wet and oven dried at 60°C and used directly in PBX formulations (Figure 2).

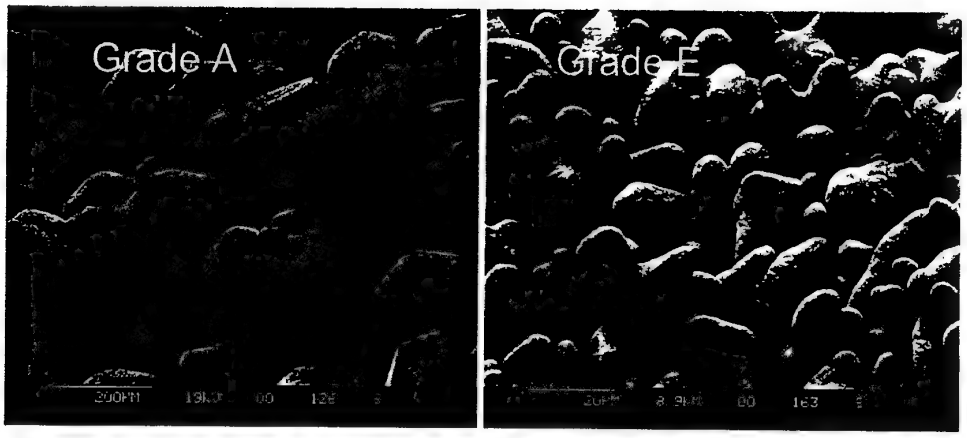


Figure 2. SEM of RDX, Grade A and Grade E

3.3 Preparation of Isocyanate Cured PBXs

PBX formulations are listed in table 1 and were prepared using a Baker Perkins 1 pint (473.2 mL) explosive mixer. Ingredients were added in the following order, with the mix method detailed in Appendix B:

1. PolyGLYN/Plasticiser,
2. RDX (pre-mixed grades A and E), three increments,
3. Isocyanate cross-linking agents.

The PBX systems were cured with a 50:50 N100/IPDI mixture at a ratio of 1.1:1 isocyanate/polymer hydroxyl with the addition of 5 ppm dibutyl tin dilaurate as catalyst. PBX formulations were prepared by first degassing polymer and plasticiser in a vacuum oven at 70°C for 16 hours. The RDX was then mixed into the binder in incremental additions followed by isocyanate curing agents and incorporated for 20 mins. The PBX was then cast into pre-heated steel moulds (250 mm x 25.4 mm diameter, Figure 3) and left to cure in an oven at 70°C for 7 days.

Table 1: Formulation Compositions (%). All formulations contain 5 ppm dibutyl tin dilaurate as catalyst

Formulation	RDX (A/E)*	PolyGLYN	K10	GLYN oligomer	N100/IPDI
ARX-3001 M5 (75%)	75	10.5	12.5	-	2.0
ARX-3001 M6 (77%)	77	9.6	11.5	-	1.9
ARX-3005 M1 (77%)	77	9.6	-	11.5	1.9
ARX-3006 M1 (79%)	79	9.0	-	10.5	1.5
Composition B	59.5% RDX, 39.5% TNT & 1% wax (melt-cast)				

* a bimodal RDX distribution of 60/40 Type A/E was used to maximize casting density.

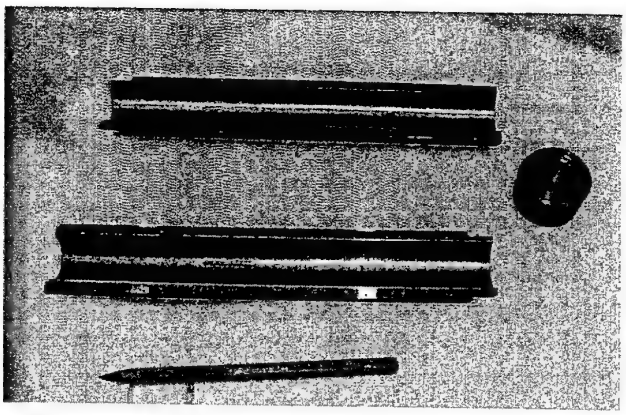


Figure 3: Experimental Moulds used in PBX Formulation Studies

3.4 Instrumentation

3.4.1 Density

Absolute densities were determined using a Quantachrome Helium Ultrapycnometer 1000 by the procedure given in test 1 (absolute density determination) of [4]. Ultra high purity Helium gas as supplied by BOC Gases was used. The pycnometer was set for a maximum of 10 analyses. Volume of the sample is calculated via the following equation:

$$V_s = V_c - \frac{V_{exp}}{\frac{P_1}{P_2} - 1}$$

where V_s = sample volume
V_c = cell volume
V_{exp} = expansion volume
P_1 = initial pressure
P_2 = pressure after expansion

Density is automatically calculated by the pycnometer.

3.4.2 Viscosity

Viscosity measurements were conducted on a Brookfield DV-1 HBT digital viscometer with a helipath stand (model D) and Type C t-bar spindle. Viscosities were determined on *uncatalysed* samples to minimise the effects of rapid curing. Recordings were made at a single point 30 s after the helipath started its descent at all rotation speeds possible without the viscometer going off-scale. Viscosity/temperatures profiles were obtained at 30, 40, 50 and 60°C at various speeds.

3.4.3 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) analysis was performed using a Perkin Elmer Pyris 1 under nitrogen purge in closed aluminium pans. Glass transition temperatures (Tg) were measured by cooling the sample to -120°C for 1 minute and then heating to 20°C at 5°C per minute. The Tg was taken as the point of inflection of the specific heats for the glass and rubber phases of the binder and is an average of two measurements. The freezing point of water was used as the reference for low temperature work. High temperature decomposition behaviour was measured by heating from 25 to 500°C at 5°C per minute with Indium metal as reference (156.7°C).

3.4.4 Scanning Electron Microscopy

Electron micrographs were performed on a Philips XL30 Field Emission Scanning Electron Microscope (SEM) using a secondary electron detector. Samples were analysed after gold sputtering and imaged at 5-10 kV to prevent charging and to improve contrast.

3.5 Hazards and Mechanical Properties Testing

3.5.1 Rotter Impact Sensitiveness

Impact sensitiveness was determined on a Rotter apparatus [5]. Samples were prepared from cast-cured sheets of the material under investigation using a scalpel to cut individual discs each of about 30 mg. Each sample was then placed in a brass cap, allowed to stand overnight in a desiccator, then fitted over a polished steel anvil and impacted by a 5 kg weight falling from a preset height.
Go/no go was determined by the evolution of gas, a positive result being recorded for >1 mL. Impact height was varied in a Bruceton procedure with a total of 50 caps being tested.
The resulting figure of insensitiveness (F of I) is quoted relative to RDX, Grade F = 80 and is rounded to the nearest 5 units. Gas evolution represents the average of all positive results.

3.5.2 Friction - BAM Test

The BAM test measures friction values by applying a thin film of sample to a ceramic tile and lowering the friction peg [6]. The maximum loading was placed on the outer groove of the test arm and the peg dragged across the sample. The sample was observed for any sign of ignition, spark or smoke. The test was repeated with decreasing loadings until six repetitions with the same loading provided no evidence of ignition. This loading (N) is reported as the minimum required for ignition.

3.5.3 Temperature of Ignition

Temperature of ignition (T of I) was determined on an instrument built to specification for the ERDE T of I test [5]. Samples of 200 mg in glass test tubes were heated at 5°C/min till ignition or fast burn occurred, as defined by first visible signals such as smoke/flame or audible hiss/bang. The T of I is the lowest temperature at which this event occurs.

3.5.4 Electrostatic Discharge, ESD

This test is performed according to the UK Sensitiveness Collaboration Committee 'Manual of Tests' [5]. The five cavities in the polyethylene strip were filled with the sample and each hole individually covered with a small square of copper foil. The strip is then connected to one side of a non-inductive capacitor and a second brass terminal connected to the other side of the capacitor and which touches the first of the small pieces of foil on top of the polyethylene strip.
A capacitor (from 0.001 to 0.1 mF) is selected using a switch that connects to an earth. The capacitor is charged to a potential of 9.5 kV, giving a stored energy of 4.5 J, 0.45 J or 0.045 J. The test is initiated by applying a pulse that causes the potential of the selected capacitor to form across the sample spark gap.

3.5.5 Vacuum Stability

Duplicate 2.0 g samples of the formulations were placed in glass sample tubes which were attached to a mercury-filled manometer and evacuated [7]. The sample tubes were then placed in a heater bath at 100°C and a 1 h period was allowed for temperature equilibration. The volume of gas evolved was monitored for 48 h at 100°C and is the average of duplicate samples.

3.5.6 Hardness

The ASTM-D2240 method was used to assess Shore "A" hardness [8]. A Shore A-2 Durometer with a Shore Conveloader test stand, which uses a hydraulic cylinder to control the rate of application of the indenter to the sample, was used with the standard 1 kg weight.
Hardness measurements were performed on the top surface at a distance of between 6 mm and 12 mm from the edge. Variations in hardness along a surface from centre to edge were found to be insignificant for respective surfaces. Five indentations per assessment were performed at ambient room temperature and results averaged.

4. Results

4.1 Physico-chemical Properties

4.1.1 Energetic Binder System

Energetic binder systems such as PolyGLYN with K10 or GLYN oligomer plasticisers can be incorporated efficiently into PBX formulations to give a PBX with expected IM characteristics and increases in detonation parameters such as detonation velocity and detonation pressure. Such improvements are a direct result of the properties of the energetic binders component. Physico-chemical properties of the binder components as measured by density, DSC and vacuum stability tests are displayed in Table 2. Components all contain good decomposition temperatures and low Tg coupled with good compatibility.

Table 2: Physico-chemical Properties of PolyGLYN, GLYN Oligomer and K10

Properties	PolyGLYN [9]	GLYN oligomer	K10 [10]
Density, g/cm^3	1.46	1.39	1.39
T_g, °C (DSC)	-35	-64	-66
T_m, °C (DSC @ 5°C/min)	195.0	188	250
ΔH_f, kJ/mol	-284.2	-789.5	-87, +126
Stability, mL/g# (Vacuum Stability Test)	0.93	1.84	1.52

Vacuum stability testing performed at 100°C for 48 hours.

4.1.2 PBX Properties

Physico-chemical properties are presented in Table 3. The PBXs all have close to theoretical maximum density with good hardness results. The GLYN oligomer plasticised PBXs (ARX-3005 M1 and 3006 M1 formulations) show the highest hardness values.

Thermal properties of the binders have been measured by DSC (differential scanning calorimetry) to determine the onset of decomposition, T_m and the glass transition point temperature, T_g or the point at which the PBX converts from a rubbery binder state to a glassy state. All PBX formulations have workable low T_g's and relatively high decomposition temperatures, T_m making their use in munition systems attractive. Figure 4 shows a typical DSC trace for ARX-3006 M1. For hardness tests, ARX-3006 M1 (79% RDX loading) shows the highest hardness values with the lowest Tg recorded (42.3°C), the hardness test values of 59 implying good mechanical properties.

Table 3: PBX Properties of ARX-3001, 3005 and 3006 Formulations

PBX	Composition	Density, g/cm³	Hardness	Tg, °C	Decomp. Temp, °C	Vac. Stab., mL/g
ARX-3001 M5	RDX 75% PolyGLYN K10	1.67	34	-38.9	201	0.46
ARX-3001 M6	RDX 77% PolyGLYN K10	1.68	51	-38.0	208	0.88
ARX-3005 M1	RDX 77% PolyGLYN GLYN olig.	1.68	56	-40.9	208	0.74
ARX-3006 M1	RDX 79% PolyGLYN GLYN olig.	1.68	59	-42.3	209	0.61

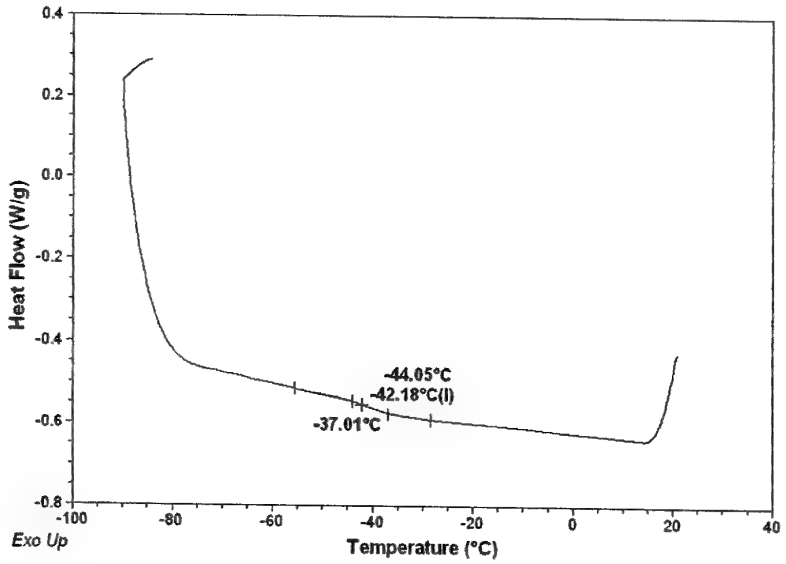


Figure 4. Sub-ambient DSC Trace of ARX-3006 M1 (79% RDX loading)

If we consider current UK operational requirements for the air carriage of munitions (ranges from -55°C to 71°C [10]), then these PBXs show good thermal stability and easily reach the upper operational limit. However, it is at the lower operational limit of -55°C that most energetic binders fail to perform, and this is where free chain mobility

becomes hindered below the polymer's glass transition temperature. This may necessitate the use of better processing aids to plasticise energetic binders for air carriage ordnance.

4.1.3 Compatibility Testing

Vacuum stability tests for all PBX formulations were carried out at 100°C for 40 hr (Table 3). The acceptance criteria for thermal stability by this method is taken as less than 2 mL/g and is based on Test Series 7 of the United Nations' "Recommendations on the Transport of Dangerous Goods" [11]. All PBX formulations show good stability when fully cured. ARX-3001 M6 with 77% RDX loading exhibits the highest gassing rate of 0.88 mL/g, well under the acceptance criteria.

4.2 Viscosity

Viscosity measurements were conducted on *uncatalysed* mixes to minimise the effects of rapid curing. A helipath stand was used to eliminate any channelling effects and thus provide consistent viscosity measurements. All formulations display typical non-Newtonian, pseudoplastic flow behaviour with decreasing 'apparent viscosity' at increasing spindle shear rates (Figure 5). Interestingly, GLYN oligomer plasticised PBXs have lower apparent viscosities at higher spindle speeds (5 RPM) over K10 plasticised PBX systems (ARX-3001). ARX-3006 M1 containing 79% RDX displays high viscosity approaching over 10 000 poise, and when coupled to the low impact sensitivity results, may well be at the upper limit of castability and fulfilment of IM criteria. Further formulation of ARX-3006 M1 and sensitivity testing is required.

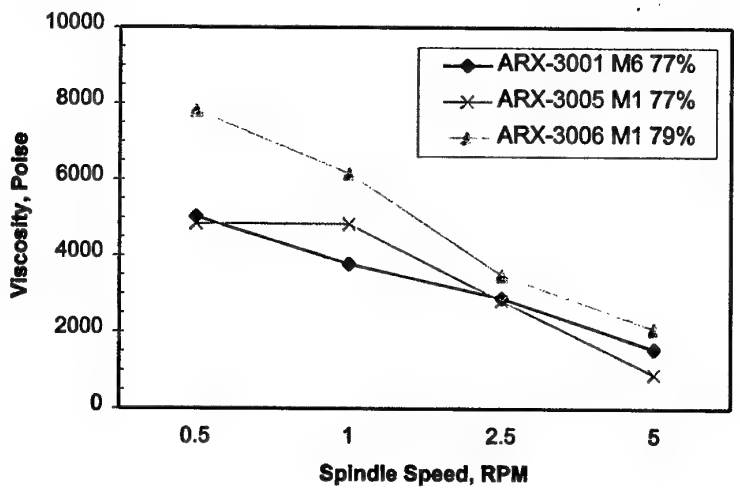


Figure 5: Viscosity Profiles of ARX-3005/6 at increasing spindle shear rate (Type C spindle, 60°C)

Figure 6 shows the change in viscosity with temperature at a constant spindle rate (0.5 RPM) for the three compositions. ARX-3001 M6 and ARX-3005 M1 at 77% RDX loading display similar viscosities that overlap at higher temperatures (60°C). However, ARX-3006 M1 at 79% RDX loading has a higher viscosity than both 77% compositions. At the same oxidant level (RDX), the GLYN oligomer plasticised PBXs appear to offer improvements in mix viscosity and processability over K10 plasticised systems.

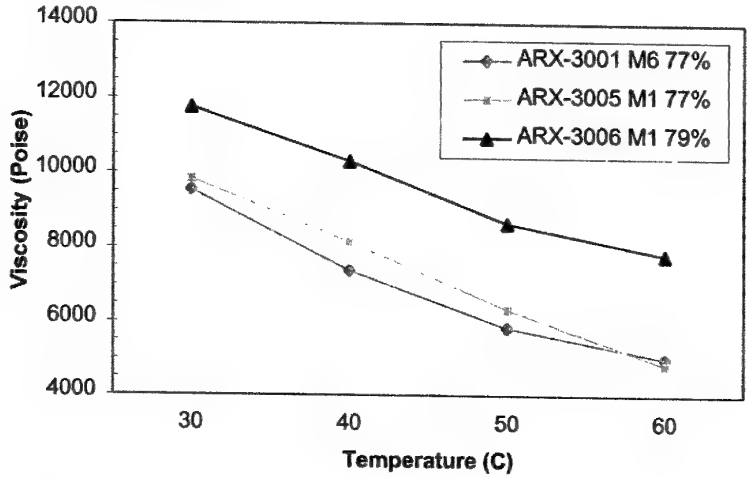


Figure 6: Viscosity/Temperature Profiles for ARX-3001/3005/3006

The viscosity/temperature profile as obtained for the uncured PBXs is highly dependent upon a number of instrument variables including viscometer and spindle type, shear rate used, sample containment and experimental error. Effort must be made to ensure that viscosity profiles are recorded with identification of the exact equipment and technique.

4.3 Small-scale PBX Hazards Assessment

Small-scale hazard assessment data for all formulations are shown in Table 4. PBX formulations are compared to the reference formulation - Composition B. All formulations showed within variance friction values (BAM) comparable with Composition B reference values. For impact data, K10 plasticised PBXs (ARX-3001 M5 & M6 series) show reduced impact sensitiveness over Composition B whereas GLYN oligomer plasticised PBXs (ARX-3005 M1 and 3006 M1) show a increase in impact sensitiveness from 130 to 100 (RDX=80). Such a result may imply poor impact properties for these formulations and further testing is required. No evidence of reaction to electrostatic discharge was observed and stable temperature of ignition values were also obtained.

Table 4: Small-scale Hazard Assessment

Formulation	F of I#	BAM, N	T of I, °C	ESD, J*
ARX-3001 M5 (75%)	160	96	197	No ignition at 4.5 J
ARX-3001 M6 (77%)	130	112	203	No ignition at 4.5 J
ARX-3005 M1 (77%)	100	112	202	No ignition at 4.5 J
ARX-3006 M1 (79%)	100	120	202	No ignition at 4.5 J
Composition B	130	112	212	No ignition at 4.5 J

RDX = 80.

* Lowest energy level (4.5, 0.45, 0.045 J) at which an event occurs is reported.

4.4 PBX Performance Assessment

PBX formulations containing both K10 and GLYN oligomer have been successfully prepared with 75, 77 and 79% RDX loadings (see Figure 7 for a comparison of plasticiser effect on PBX quality). Figure 7 clearly highlights the differences between the two plasticisers on charge quality. The K10 PBX (left of Figure 7) contains voids and plasticiser migration is evidenced from the colour variation from either end of the charge. Test charges were fired in triplicate and average performance results presented (see Appendix C for a full listing of shots fired). Velocity of detonation (VoD) and detonation pressure (P_{CJ}) for all PBX formulations were determined using unconfined cylindrical charges (25.4 mm diameter, 150 mm length) cast cured to a density of 1.68 g/cm^3 (calculated from charge dimensions and helium pycnometry). Shots were boosted with 50:50 pentolite cylinders (25.4 mm X 25.4 mm diameter) and initiated with Resi 501 EBW detonators. VoD was determined by high-speed streak photography and a typical representation of a PBX streak record is given in Figure 8. P_{CJ} was estimated via dent tests on cylindrical PBX charges and fired into stacks of mild steel witness plates (50 mm thick) and referenced to Composition B charges of identical dimensions [12]. Dent depths were measured on a Sheffield Endeavor coordinate measuring machine (Model 9.12.7), shown in Figure 9.). For calibration standards, a series of Composition B charges (4 shots at 150 mm length x 25.4 mm diameter) were fired to give an average dent depth of 4.557 mm (Appendix C). Calculated VoD and detonation pressures were obtained using the Cheetah program [13].

Table 5: Experimental and Calculated Performance Parameters (Average Values)

PBX	Experimental		Calculated	
	VoD, (m/s)	P_{CJ}, (GPa)	VoD, (m/s)	P_{CJ}, (GPa)
ARX-3001 (75%)	8037 (± 32.2)*	27.1	7939	26.1
ARX-3001 (77%)	8085 (± 32.3)	27.5	8097	27.4
ARX-3005 (77%)	8151 (± 32.6)	27.9	8159	27.6
ARX-3006 (79%)	8159 (± 32.3)	28.4	8233	28.2
Composition B	7586 (± 30.3)	24.0	7630	24.7

* standard deviation values given in brackets, quoted in m/s.

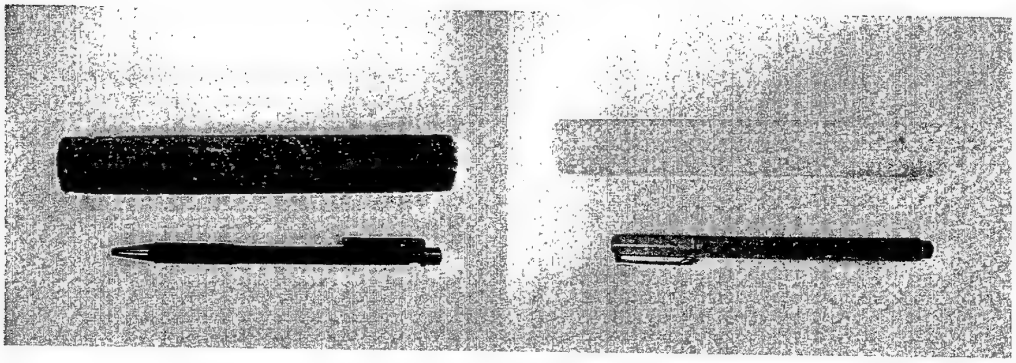


Figure 7: PBX Plasticised with K10 and GLYN Oligomer (77% RDX Filled)

Figure 8: Streak record of ARX 3001/M6 (75% RDX) velocity of detonation profile

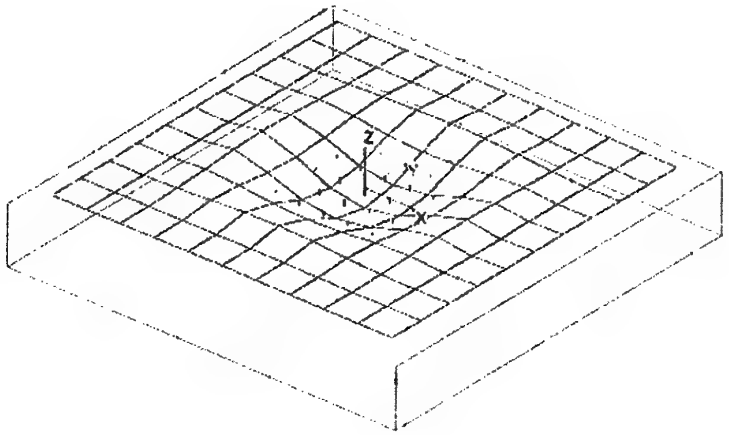


Figure 9: Representative Dent Depth Measurement of Witness Plates as Measured by a Sheffield Endeavor Model 9.12.7

High VoDs were obtained for the K10 based ARX-3001 M5 & M6 (75 & 77% RDX) and compare well to Cheetah predictions. Differences between experimental and calculated VoDs where within experimental error (i.e. for ARX-3001 M5, 75% RDX, experimental value of 8035 m/s *c.f.* 7939 m/s for calculated and for 77%, 8086 *c.f.* 8097 m/s). ARX-3005 M1 (77% RDX loading) gives very good agreement to Cheetah calculations (8151 m/s *c.f.* 8159 m/s) while ARX-3006 M1 (79% RDX) gives lower than expected values when compared to Cheetah calculations, and may be attributed to casting variations.

Regardless of minor variations from Cheetah calculations, all PBXs comprising energetic binder systems show improvements in velocity of detonation results over PBXs containing inert binders and over Composition B.

For comparison, several inert compositions [10] are compared to the energetic PBXs developed at WSD (Table 6). Comparisons are made to PBXN-106 [15] and PBXN-107 [14], both cast-cured US navy compositions. Comparisons are also made to two inert binder compositions containing HMX, which by virtue of HMX's extra energy output, should give extra performance over RDX analogues. Superior performance is seen in the energetic binder PBXs over the inert HMX containing systems and PBXN-106 [15] and PBXN-107 [14]. The energetic binder containing PBXs show excellent performance parameters when compared to the formulations shown in Table 6. PBXN-107 has a VoD of 8090 m/s which is lower than that obtained for ARX-3005 M1 VoD of 8160 m/s, and which has only 77% RDX loading compared to the 86% RDX loading for the PBXN-107 composition. This represents an increase of around 10% in explosive performance parameters, and is attributed to the direct incorporation of energetic binders into the PBX. At a 75% RDX loading, the PBX formulation ARX-3001 M5 displays an energy increase of 2.5% (7804 m/s *c.f.* 8037m/s) over PBXN-106, which contains an inert polymer coupled with an energetic plasticiser at 75% RDX loading.

Table 6: Performance Comparisons of Inert and Energetic Binder Systems

PBX	VoD (calc, m/s)	VoD (exp, m/s)
ARX-3001 (75%)	7939	8037
ARX-3001 (77%)	8097	8086
ARX-3005 (77%)	8160	8159
ARX-3006 (79%)	8230	8086
PBXN-106†	7800	7840
PBXN-107^	7690	8090
HTPB/IDP*/HMX [10] (7.5:7.5:85)	8050	-
HTPB/DOS#/HMX [10] (7.5:7.5:85)	7880	-

† PBXN-106 comprises 75% RDX with a polyethylene glycol/BDNPA-F binder system cured by isocyanate cross-linkers [15].
^PBXN-107 comprises a cast-cured PBX filled with RDX (86%) and polyacrylate binder (14%) [14].
* IDP = isodecyl pelargonate plasticiser.
# DOS = dioctyl sebacate plasticiser.

Apart from enhancing PBX performance parameters such as VoD and P_{CJ}, energetic binders allow for set performance levels to be achieved with lower energetic solids loading which should further improve IM characteristics.

4.4.1 Chapman-Jouguet Pressure

Detonation pressure (P_{CJ}) was estimated from dent tests and compared to open-cast Composition B charges [16]. The results for all PBXs measured closely match that obtained from the theoretical relationship derived by Fickett and Davis from simple one-dimensional detonation theory [17]:

$$P_{CJ} = \frac{\rho D^2}{\gamma + 1}$$

where ρ = density (g/cm^3)
D = limiting velocity of detonation (km/s)
γ = ratio of the specific heats of the detonation product gases.

The above relationship assumes that the ratio of the specific heats of the detonation product gases, γ is taken to be equal to 3 (a good approximation for most high explosives close to the maximum theoretical density). Applying this relationship gives quite good comparison to the dent depth pressures and to the Cheetah predictions as shown in Table 7 (a full listing of results for experimentally measured and calculated detonation pressures can be found in Appendix C). CHEETAH 2.0 is a computer software program that utilises traditional Chapman-Jouget thermodynamic detonation theory to accurately model and predict performance of new explosive compositions as

well as ideal explosives and serves as a useful tool for comparison to experimental and one-dimensional theory [13].

Table 7: P_{CJ} Data from Experimental, 1-Dimensional Theory (Fickett & Davis Relationship) and CHEETAH 2.0 Thermochemical Code for PBX Energetic Binder Systems

PBX	P_{CJ}, GPa		
	Experimental*	1-D Theory	CHEETAH 2.0 Thermochemical Code
ARX-3001 (75%)	25.55	27.06	26.11
ARX-3001 (77%)	27.24	27.57	27.43
ARX-3005 (77%)	28.91	27.95	27.62
ARX-3006 (79%)	27.85	27.51	28.21

* based on dent depth measurements and referenced to Composition B.

For CHEETAH 2.0 thermochemical code, errors for the CJ pressure are typically of the order 10% and are based on PETN measurements [18]. Thus, if we assume an overall error of 10% per formulation, we find that for all PBX formulations, the three CJ pressures are within error for each PBX.

For the ARX-3001 formulations which are based on K10 plasticiser, both the experimental (25.55 GPa) and one-dimensional theory values (27.06 GPa) show good agreement to the CHEETAH 2.0 prediction of 26.11 GPa. For the formulation containing 77% RDX, the P_{CJ} was 27.57 GPa and shows good agreement to Cheetah predictions as well as to the experimental dent depths (P_{CJ} of 27.43 GPa and 27.24 GPa, respectively).

For the GLYN oligomer based systems, the ARX-3005 and 3006 formulations also give good agreement within specified error. The high experimental result for ARX-3005 (28.91 GPa) for 77% RDX is reflected in its VoD result (Table 5) which is correspondingly higher than the 79% ARX-3006 PBX. This result clearly highlights the further work that is required for the ARX-3006 PBX formulation.

5. Conclusions and Recommendations

To achieve high lethality missile systems requires maximum performance from the warhead. Current missile systems such as ASRAAM use cast-cured inert binders or pressed PBXs to achieve the desired energetic performance. We have developed several PBX formulations that contain energetic binders with high loadings of RDX that may offer potential application in these systems. Incorporation of energetic binders should allow for the design of PBXs with IM-compliance and without the loss of performance experienced by conventional inert binder containing PBXs. The binder systems comprise a polyGLYN binder matrix with a single plasticiser, either K10 or GLYN oligomer. Good physico-chemical properties have been obtained for all PBX formulations, including density, hardness and thermal properties. Thermal

characteristics of the PBX formulations reveal low glass transition points and relatively high decomposition temperatures allowing for their use as binders in munitions. In addition, compatibility testing shows excellent compatibility of all ingredients tested.
Performance assessment of the two different binder systems (PolyGLYN plasticised with either K10 or GLYN oligomer) show good comparison to theoretical calculations as predicted by the Cheetah computer program except for ARX-3006 where more experimental data is required. Performance parameters obtained for the GLYN oligomer plasticised systems were slightly greater than the K10 systems. When this is coupled with the migration data, the GLYN oligomer shows better explosive composition properties than K10 plasticised systems.
Sensitiveness results show reduced hazards, especially when compared to other inert systems. However, PBX formulations ARX-3005 M1 and 3006 M1 show an increase in impact insensitiveness. In addition, conjecture regarding the impact hazard data for the GLYN oligomer exists and further research needs to be conducted to determine the sensitivity properties of this plasticiser
This Technical Report is part of on-going research into high performance missile fills comprising energetic binder systems, and several recommendations for further work include:

1. Incorporation of HMX in place of RDX to further boost performance.
2. Assessment of composition sensitivity including shock and thermal.
3. Further work into rheological investigations on new formulations needs completing.
4. Further performance assessment work is required on PBX formulations, in particular those containing the GLYN oligomer plasticiser.
5. Optimisation of final PBX formulations and final characterisation.

Not only do energetic binders enhance a PBX's performance, they also allow a set performance level to be achieved at lower explosive solids loadings, with an expected improvement in IM characteristics. With the growing need for IM compliant munitions, it is likely that systems such as ASRAAM may very well require incorporation of energetic binders in cast-cured compositions that offer improved PBX sensitivity and energy.

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Appendix A: PBX Nomenclature

Explosive compositions developed by explosives group, WSD are recorded and classified according to binder type used. The explosive composition is given the prefix ARX (Australian Research eXplosive) and one of the following classes used:

ARX-1000 - 1999	Pressed compositions
ARX-2000 - 2999	Inert binder compositions
ARX-3000 - 3999	Energetic binder compositions
ARX-4000 - 4999	TNT-based and other melt-castable compositions
ARX-5000 →	Yet to be assigned

These composition numbers are used in conjunction with an **M** suffix for indicating minor composition variations (eg a 1 or 2% increase in RDX content, or the use of a different isocyanate). Changes in the mix method *do not* necessarily justify the allocation of another **M** number. Thus a new energetic binder composition would be ARX-3000/M1. Increasing the RDX content slightly or the use of a different grade would produce ARX-3000/M2 and so on. Assignment of new ARX numbers for compositions in progress is at the discretion of the experimentalist, however, a new number should *not* be assigned unless the composition has moved significantly away from the original formulation. Inert compositions are designated using the suffix **I**. Therefore an inert HTPB composition would be numbered ARX-2000I/M1.

Appendix B: Method of PBX Manufacture

The following mix procedure was used to formulate ARX 3001-M6 (75% RDX loading) (mix number EG 0162, Cast No. 025) and is indicative of all mixes performed. The formulation below consists of RDX (75%, Grade A/B 60:40), PolyGLYN (10.5%, Bx-31), K10 (12.5%), IPDI (0.35%) and Desmodur N100 (1.7%). DBTDL was used as a cure catalyst at 5 ppm concentration with respect to the PolyGLYN pre-polymer.

1. Degas/dry PolyGLYN and K10 plasticiser at 60°C under vacuum for 3-4 hours in the mixer.
2. Add RDX (premixed grade A and E) in incremental lots (3 increments) with mixing times of 10 mins for each increment. Total mix time = 30 mins at 15 RPM.
3. Add IPDI and Desmodur N100 and mix for 5 mins at 20 RPM.
4. Scrape down blades and mix for a further 15 mins at 20 RPM.
5. Remove pre-heated moulds and assemble, vacuum cast into the moulds to ensure minimum heat loss.
6. Vibrate mould to ensure maximum solids loading.
7. Place mould under vacuum again and cycle until gas evolution ceases.
8. Remove from vacuum and place in oven at 70°C and cure for 7 days.

Appendix C: PBX Experimental and Theoretical Performance Parameters

PBX	Density, (g/cm^3)	TMD (g/cm^3)	Experimental VoD (m/s)	Experimental P_{CJ} (GPa)	Theoretical P_{CJ}# (GPa)
ARX-3001 (75%)		1.677			
Shot 1	1.675	99.8%	8206 (± 32.8)*	24.79	28.19
Shot 2	1.670	99.9%	7892 (± 31.5)	23.82	26.00
Shot 3	1.669	99.5%	8085 (± 32.3)	26.28	27.27
Average			8037 (± 32.2)	25.55	27.15
ARX-3001 (77%)		1.697			
Shot 1	1.685	99.3%	8497 (± 33.9)	27.55	30.41
Shot 2	1.680	98.9%	7951 (± 31.8)	26.94	26.55
Shot 3	1.678	98.8%	7808 (± 31.2)	26.36	25.57
Average			8085 (± 32.3)	27.24	27.51
ARX-3005 (77%)		1.700			
Shot 1	1.700	100%	8138 (± 32.5)	29.05	28.15
Shot 2	1.673	98.4%	8164 (± 32.6)	28.77	27.87
Shot 3	1.676	98.6%	7923 (± 31.0)	24.93	26.89
Average			8151 (± 32.6)	27.58	27.95
ARX-3006 (79%)		1.700			
Shot 1	1.700	100%	8159 (± 32.6)	28.43	28.29
Shot2	1.699	99.8%	8012 (± 32.0)	27.28	27.26
Average			8085 (± 32.3)	27.85	27.51
Comp. B		1.68			
Shot 1	1.68	100%	7507 (± 30.0)	24.02	23.66
Shot 2	1.66	98.8%	7605 (± 30.4)	24.65	24.00
Shot 3	1.68	100%	7646 (± 30.6)	24.98	24.55
Average			7586 (± 30.3)	24.55	24.07

* standard deviation values given in brackets, quoted in m/s.

\# derived from the Fickett & Davis relationship based on one-dimensional theory.

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19. ABSTRACT

In an effort to comply with Insensitive Munitions (IM) criteria together with the expectation of increasing the warhead performance against specified targets, two part energetic binder systems comprising an energetic polymer and plasticiser that offer promise for future use in PBX (polymer bonded explosive) fills in high performance, tactical missiles have been investigated. Warhead fills within modern missiles such as ASRAAM (Advanced Short Range Air-to-Air Missiles) typically contain cast-cured PBXs comprising high energetics loadings in an inert binder matrix. The use of the inert binder, which comprises around 20% of the final formulation, dilutes the final energy output of the PBX. To this end, several energetic binder formulations have been developed that may offer potential use in ASRAAM type missiles. By use of energetic binders systems comprising polyGLYN and K10 or GLYN oligomer plasticiser, increases in performance parameters were observed. This technical report details the formulation of several PBXs developed to maximise casting density and processibility for potential use in ASRAAM warheads that may offer improved IM properties.